

Electrochemical Detection of Nitroaromatics using the Boron-Doped Diamond Electrode

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Due to growing environmental concerns, nitroaromatic compounds have been targeted for monitoring because of their inherent biological toxicity. There is significant motivation for the development of rapid, stable, inexpensive and robust sample analysis protocols for this class of analytes in both the military and civilian sectors. The use of capillary electrophoresis (CE) systems coupled with electrochemical detection provides many attractive features toward achieving the above goal. The electrochemical reduction mechanism of the nitro group on these compounds has been described by Rubinstein.¹ Boron-doped diamond electrodes have been shown to offer robust electrochemical properties with respect to the fouling associated with electrochemical organic reactions^{2,3} and provide an obvious choice for the present task at hand. Our long-term goal is to develop a microchip separation method for these contaminants that uses diamond electrodes and amperometric detection.

One complication for the analysis of nitroaromatics, such as nitrotoluenes, is the absence of a formal net charge. Therefore, separation of nitrotoluenes cannot be achieved through capillary zone electrophoresis (CZE) and requires the use of micellar electrokinetic capillary chromatography (MEKC). It has been shown that micelles can have a profound influence the reduction mechanism, specifically for the hanging mercury drop electrode.⁴ Thus, a study of the electrode response for nitrotoluene in the presence of micelles is of great importance in order to achieve optimum signal-to-noise for such systems.

In this contribution, the electrochemical reduction of 2,4-dinitrotoluene (DNT) at microcrystalline boron-doped diamond will be reported on. The electrode response was evaluated in the presence and absence of micelles. It was found that the micelles had a significant influence on the oxygen reduction reaction at the boron-doped diamond electrode. Oxygen reduction is problematic in microchip separations as it leads to large background currents at the detection electrode. Figure 1 is 10 consecutive cyclic voltammetric scans in 25 ppm DNT in 15mM borate buffer and 15mM sodium dodecyl sulfate (SDS) at pH of 9.2. Current attenuation is observed with the increasing scan number. The sites labeled 1, 2 and 3 refer to the 2e⁻ reduction of the nitroso to the hydroxylamine, the 4e⁻ reduction of the nitro to the hydroxylamine and the 2e⁻ oxidation of the hydroxylamine to the nitroso analogs respectively.

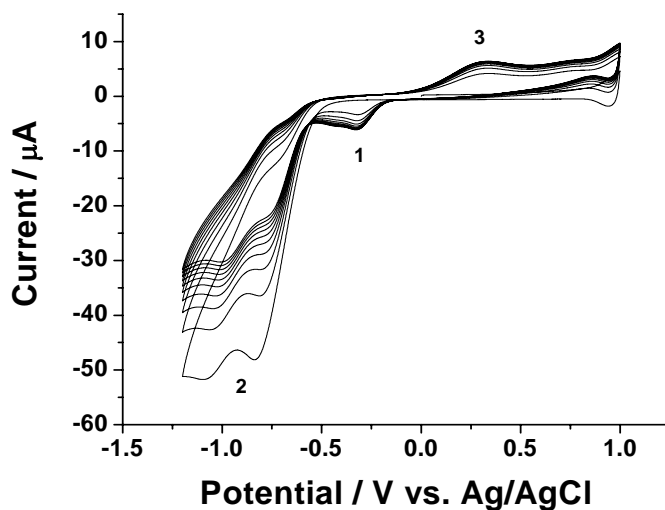


Figure 1.

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